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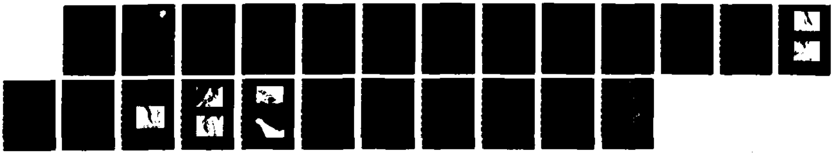

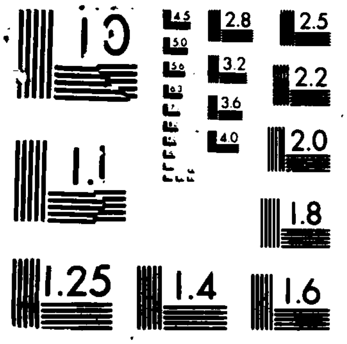
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Final Technical Report
February 1987

PHASE STABILITY OF FLUORIDE GLASSES

Catholic University of America

AD-A182 174

Catherine J. Simmons and Joseph H. Simmons

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The techniques of scanning electron microscopy, energy dispersive x-ray micro-analysis, dark-field transmission electron microscopy, and thermal analysis were combined to study the phase stability of the CdF_2-LiF-AlF_3-PbF_2 glass system. The selected composition, presumed to be the most stable, exhibited a liquid-liquid immiscibility phase transition, which led to the formation of two amorphous phases consisting of a matrix near the original glass composition and an isolated spherical phase which was richer in CdF_2 and poorer in PbF_2 than the matrix. Subsequent secondary phase separation and crystallization are observed with heat treatments.

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FORWORD

The results of our research on this contract are described in the adjoining paper submitted for publication to the Journal of the American Ceramic Society. Our results are also scheduled for presentation at the 3rd International Symposium on Halide Glasses in Rennes, France, June, 1985 (see extended abstract in the appendix) and at the Fall Meeting of the Glass Division of the American Ceramic Society in Corning, New York, November, 1985.

In this paper, we have combined the methods of transmission electron microscopy, scanning electron microscopy, x-ray microanalysis, and thermal analysis to show irrefutably and for the first time that subliquidus phase-separation occurs in some fluoride glasses, and can greatly affect crystallization processes and kinetics. These studies have opened the way for more systematic studies of phase equilibria in fluoride glasses where both phase separation and crystallization kinetics are examined in understanding the source of detrimental optical scattering losses. Such light scattering, from fully formed multiphase structures or from supercritical fluctuations in composition can, under adverse conditions, prevent the achievement of predicted low losses in fluoride glasses; therefore, an understanding of the phase-stability of these glasses and of ways to avoid phase decomposition is essential to the development of ultra-low loss communications links from these materials. Research in this area will continue both at the RADC/ESM laboratory, Hanscom AFB, Massachusetts and at the University of Florida, Gainesville, Florida.

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Phase Stability of CdF_2-LiF-AlF_3-PbF_2 Glasses†

by

Osama H. El-Bayoumi,* Catherine J. Simmons,** Edward M. Clausen, Jr.,**
Michael J. Suscavage,* and Joseph H. Simmons**

ABSTRACT

The techniques of scanning electron microscopy, energy dispersive x-ray micro-analysis, dark-field transmission electron microscopy, and thermal analysis were combined to study the phase stability of the CdF_2-LiF-AlF_3-PbF_2 glass system. The selected composition, presumed to be the most stable, exhibited a liquid-liquid immiscibility phase transition, which led to the formation of two amorphous phases consisting of a matrix near the original glass composition and an isolated spherical phase which was richer in CdF_2 and poorer in PbF_2 than the matrix. Subsequent secondary phase separation and crystallization are observed with heat-treatments.

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†This research was supported in part by the Air Force under RADC contract F19628-84-K-0036.

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**Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611

In this study two different melting techniques were used: namely, induction melting and conventional heat resistance melting techniques. Two induction melting systems were utilized. The first was an Arthur D. Litte crystal growing induction furnace (ADL) described above. It produced samples designated "slow crucible cooled" CLAP-IA. The cooling rate was estimated to be 20°C/min. The second, consisting of a modified induction furnace, recently reported, produced samples designated "fast crucible cooled" CLAP-IB. The rate of cooling was estimated to be 100°C/min. Two other glass samples were conventionally melted and cast in a brass mold to form a mainly opalescent glass CLAP-IC and a clear yellow glass CLAP-ID. The rate of cooling was estimated to be 10°C/min and 5°C/min, respectively.

Anhydrous fluorides were used as starting materials. These include CdF_2 (99.9%, Cerac), PbF_2 and LiF (Optipur, EM chemicals), AlF_3 (99.5% pure Cerac). The composition used in this study to produce samples with the four different rates of cooling consisted of 28.5 mole % CdF_2, 5.0 mole % LiF, 28.5 mole % AlF_3, and 38.0 mole % PbF_2.

Glass transition and crystallization temperatures were determined using Differential Scanning Calorimetry (DSC) at a heating rate of 10°C/min. Small bulk pieces of the glass were heated in a tube furnace at 309°C for 1 hour, 3 hours, and 16.5 hours. The furnace temperature was controlled within 1°C. A fresh fracture surface, before and after heat-treatment was immediately carbon coated and examined by SEM. The compositions of different phases were identified utilizing energy dispersion techniques. A fine powder of the glass was investigated by transmission electron microscopy (TEM) using a focused electron beam.

Results

a. Scanning Electron Microscopy

Scanning electron micrographs were taken on samples from all the different cooling rates before and after heat-treatment at 309°C for times of 1 hour, 3 hours, and 16.5 hours. Except for the fast cooled samples (IB), the results all lead to the same conclusion: the unheat-treated fast cooled samples (I-B) showed very few isolated spheres of a second phase (Fig. 1a). Unheat-treated slower cooled samples (IA) showed a larger number of the same isolated spheres, 5-10 μm in diameter, as shown in Fig. 1b. This phase was analyzed by energy dispersive x-ray microanalysis (EDX) to have a composition which is richer in CdF_2 and poorer in PbF_2 than the matrix, as shown in Figs. 2a and 2b. No information could be obtained on the AlF_3 or LiF. Assuming no change in the latter, it appeared that the CdF_2 concentration in the dispersed second phase increased from the matrix value of 38 mole % to 56 mole %, while the PbF_2 concentration dropped from 28.5 mole % to 13 mole %.

Recently reported results showed that heat-treatments at 309°C for one hour of the unheat-treated fast cooled samples (IB) caused a pronounced increase in the volume fraction of the droplet phase with no sign of crystallization. On the other hand, subsequent heat-treatments at the same temperature on slower cooled samples (IA) unexpectedly showed no change in the size or number of spheres. The micrographs in Fig. 3 show the appearance of a crystalline phase in the matrix growing from the matrix-sphere boundary. The crystalline phase exhibited in the same composition as the matrix phase SEM micrographs of the heat-treated much slower cooled samples IC and ID showed an advanced stage of the same interface matrix-droplet crystallization. The spheres were completely surrounded by the crystalline phase. SEM and EDX analysis through a fracture in the crystalline phase (Fig. 4) showed that the spherical phases inside were still amorphous (smooth) in appearance and its composition had not changed. The crystalline phase continued to grow into the matrix with no change in composition.

b. Transmission Electron Microscopy

SEM measurements yield the structure of additional phases in a glass when the sizes are large ($> 1\ \mu$). However, aside from a topographical and composition analysis, they cannot clearly identify whether a phase is amorphous or crystalline. Appearances are sometimes helpful, as in this case, where the lack of any features on the isolated spheres strongly suggest that they are amorphous. However, for a definite determination of degree of crystallinity, it is necessary to conduct diffraction measurements. The low volume fraction of the spherical phase made x-ray diffraction measurements unproductive, leaving only electron diffraction measurements in a transmission electron microscope.

In the study of phase stability of fluoride glasses, however, the transmission electron microscope does not prove to be as useful as with silicate glasses. Because of the presence of heavy transition metals and thorium, and because of the low melting point of these glasses, the samples generally adsorb the electron bean efficiently and remelt during observation due to the heating yielding very little structural information.

TEM studies were conducted on both the fast cooled unneat-treated sample (I-B) and the slower cooled sample (I-A). In the fast cooled sample we were able to avoid remelting only in very thin samples and, therefore, we were able to see the large (5-20 μ) spherical structure observed in the SEM due to its size. However, a small scale, second-phase structure was identifiable with spheres of 400-1000Å (Fig. 5). These second-phase spheres are clearly amorphous and show no electron diffraction in dark-field imaging. However, while these spheres were originally amorphous under observation in the electron beam, after a few minutes they were observed to show distinct geometrical facets and began to diffract electrons in dark field microscopy, indicating a crystal growth stage which was subsequently terminated abruptly by localized melting leaving the sample under observation in a single-phase homogenous condition.

Since the spheres observed in the TEM are too small for detection by the SEM, and those seen in the SEM are too large for TEM studies, there is no direct evidence that the phases are the same composition. However, the similar spherical appearance and thermal history in crystallization of the matrix phase are a strong indication that they originate from the same amorphous second phase in the glass with increased CdF_2 and decreased PbF_2 content.

Bright and dark field TEM studies of this glass also showed numerous micro-crystallites distributed in the sample with sizes near and below 100Å. Studies of the slow cooled sample showed an additional very small amorphous structure (Fig. 6), possibly due to a secondary phase separation.

These results indicate that many phases can develop during heat-treatment of fluoride glasses and that the competition between crystallization and liquid-liquid immiscibility occurs both in the thermodynamic and kinetic sense.

Thermal Analysis Study

One of the slowly cooled samples (1c) was studied using differential scanning calorimetry. This sample was selected because it exhibited a large density of the amorphous, second-phase spheres, with some interface crystals as well. A fast heating rate (20°C/min) was selected to minimize structural changes during heating in order to be able to relate the results of the DSC test with the structure observed in the SEM. The data obtained is shown in Fig. 7.

Near the liquidus temperature of the glass several overlapping endothermic melting peaks were observed, indicating the possible presence at least of two crystalline species. The major peaks occurred at 544°C and 557°C. At lower temperatures, two exothermic peaks were observed at 380°C and 455°C, indicating crystal growth during heating. The glass transition temperature of this glass was measured to be 275°C.

Conclusions

The CdF_2-LiF-AlF_3-PbF_2 glass system studied here exhibits liquid-liquid immiscibility. One edge of the gap is near the composition assumed to exhibit the greatest stability (28.5% CdF_2, 5.0% LiF, 28.5% AlF_3, and 38% PbF_2 by mole). The other edge of the gap appears to be in a region of higher CdF_2 concentration (56% CdF_2) and lower PbF_2 concentration (13% PbF_2). The variations in LiF and AlF_3 concentrations across the gap have not yet been determined.

It is interesting to see that the phase separation process accelerates crystallization by enhancing the nucleation process of crystals in the matrix phase. This is accomplished by either the formation of a depleted region around the amorphous droplets where the CdF_2 concentration is lowered, or by the reduction of crystalline surface energy by intersection with the interface between the amorphous phases. While crystallization occurs readily in the matrix phase by subsequent growth of crystal nuclei, the droplet phase remains amorphous to much higher temperatures. This is possibly due to a significant difference in viscosity and diffusion coefficient between the phases with the high CdF_2 phase exhibiting a lower diffusion coefficient and higher viscosity.

This glass is a clear example of the detrimental effect which liquid-liquid immiscibility can have on the resistance of a glass to crystallization. Additionally, these combined phase instabilities are expected to cause some light scattering loss in the glass. At almost any level light scattering, from such large structures as were observed in this glass, will have a detrimental effect on applications in long-distance communications, since the wavelength dependence of the scattering coefficient will follow a Mie scattering (wavelength independent) behavior rather a Rayleigh scatteromg (λ^{-4}) behavior and transmissions at longer wavelengths will not lead to reductions in losses.

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1. M. J. Suscavage, O. H. El-Bayoumi, J. J. Comer and J. A. Hoorigan, "Observation of Phase-Separation in Heavy-Metal Fluoride Glass," Amer. Ceram. Soc. Bull., 64 [3] 476 (1985).

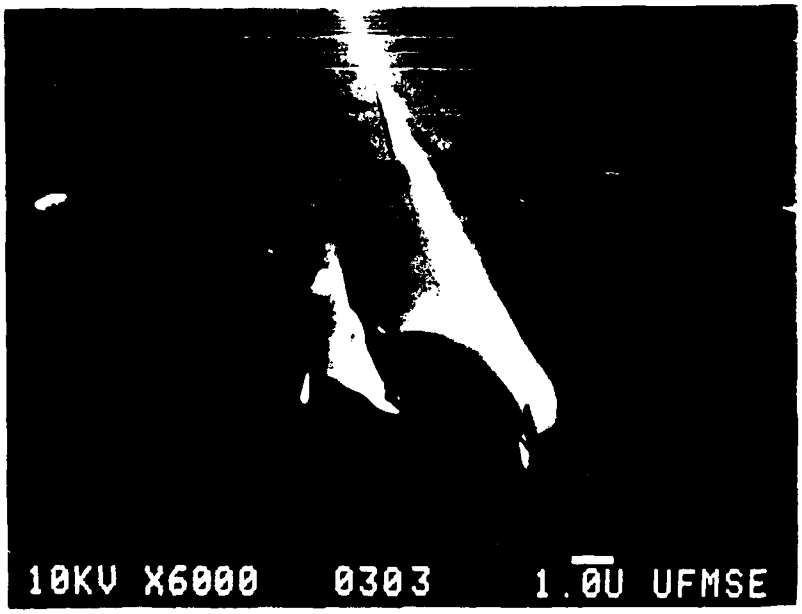
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Figure 1a - Amorphous droplet phase in rapidly quenched CLAP IB glass.

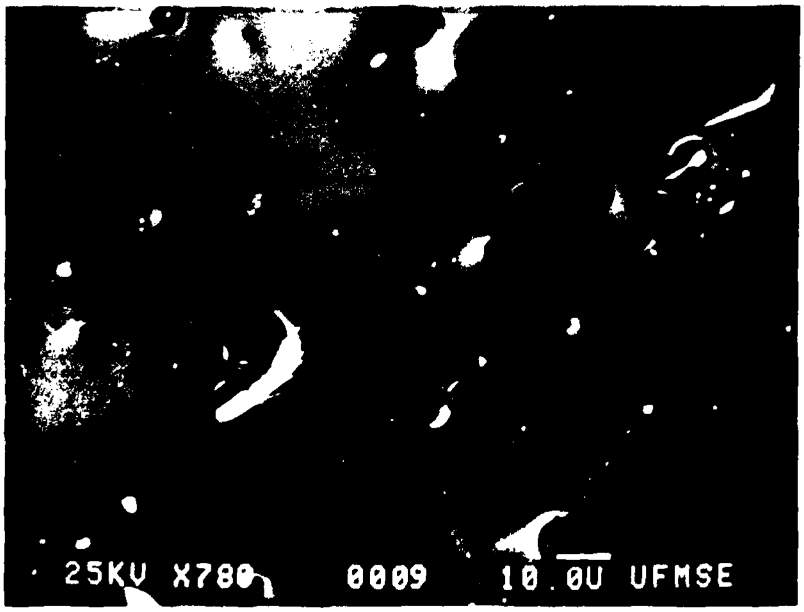
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Figure 1b - Amorphous droplets in slowly cooled CLAP IA glass.

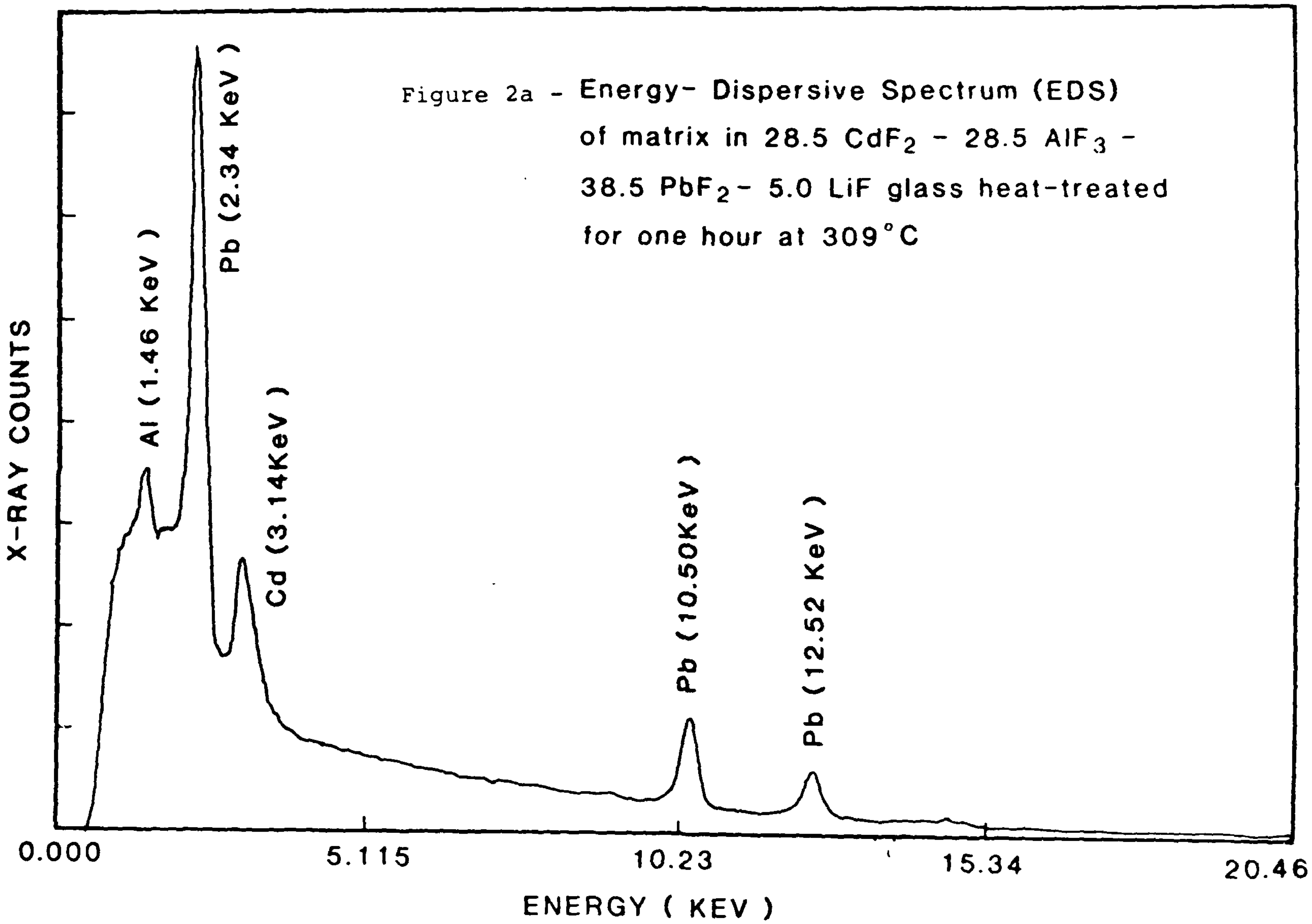

Figure 2a - Energy- Dispersive Spectrum (EDS) of matrix in 28.5 CdF_2 - 28.5 AlF_3 - 38.5 PbF_2- 5.0 LiF glass heat-treated for one hour at 309°C

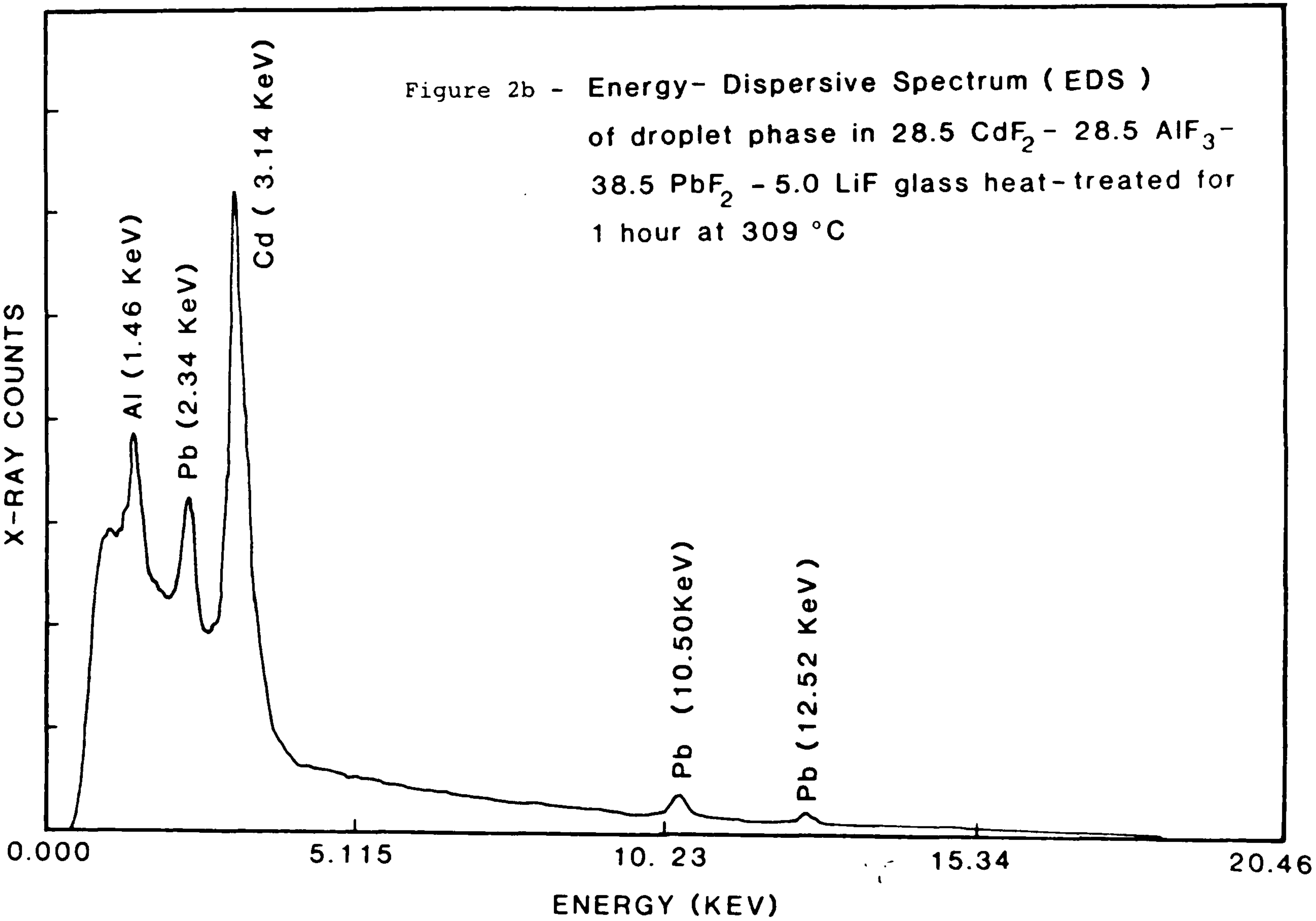

Figure 2b - Energy- Dispersive Spectrum (EDS) of droplet phase in 28.5 CdF_2 - 28.5 AlF_3 - 38.5 PbF_2 - 5.0 LiF glass heat-treated for 1 hour at 309 °C

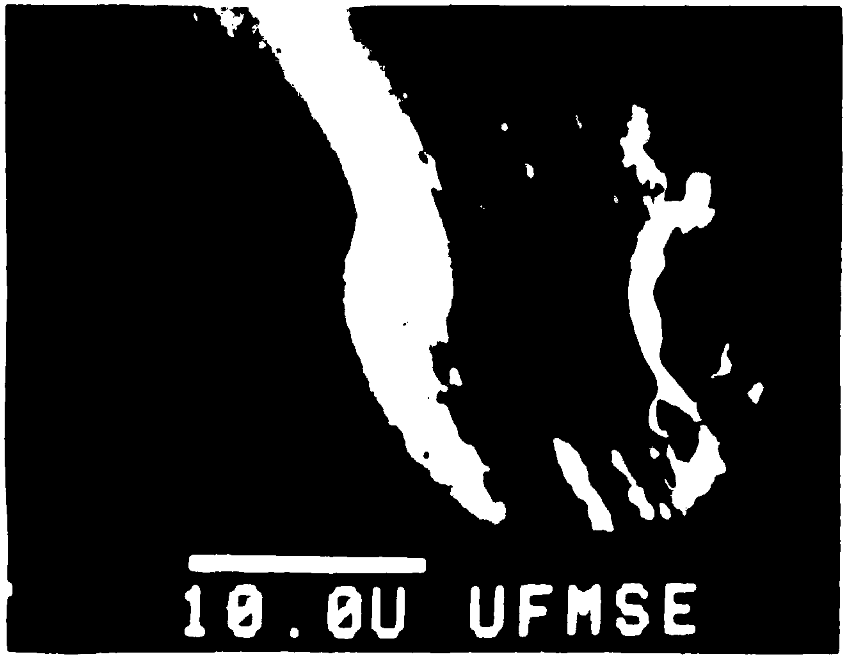

Figure 3 - Clap IA glass heat treated 1 hour at 309C showing the growth of crystals at the droplet-matrix boundary and into the matrix phase.

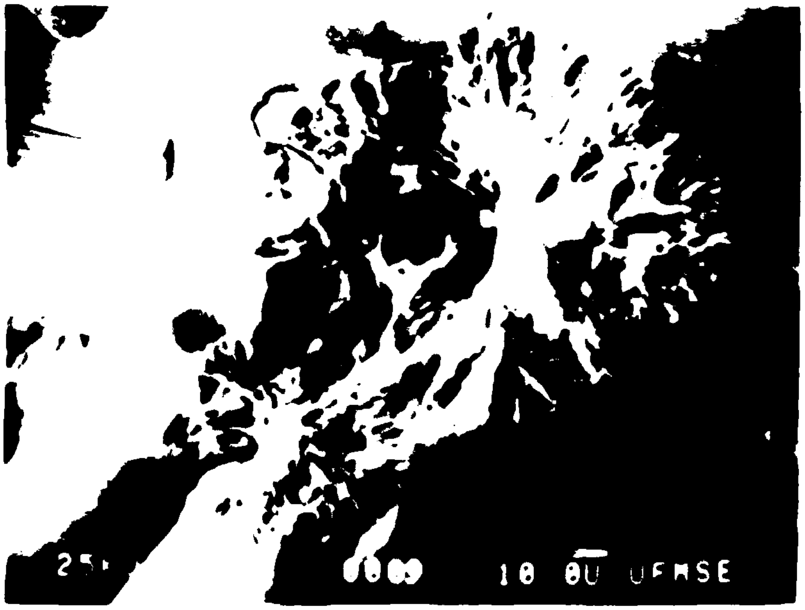

Figure 4a - Crystals with advanced development.

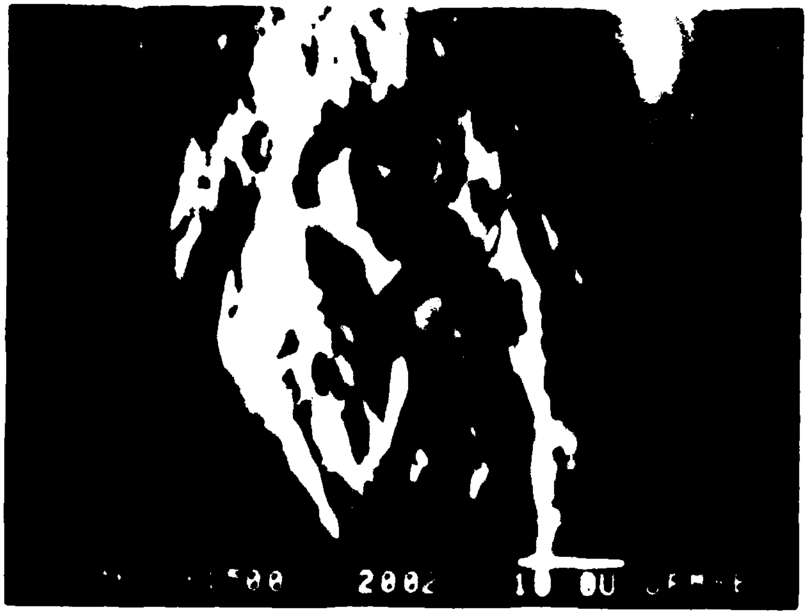

Figure 4b - EDS and SEM measurements in the crack of a crystal showed that the droplet phase was unchanged.

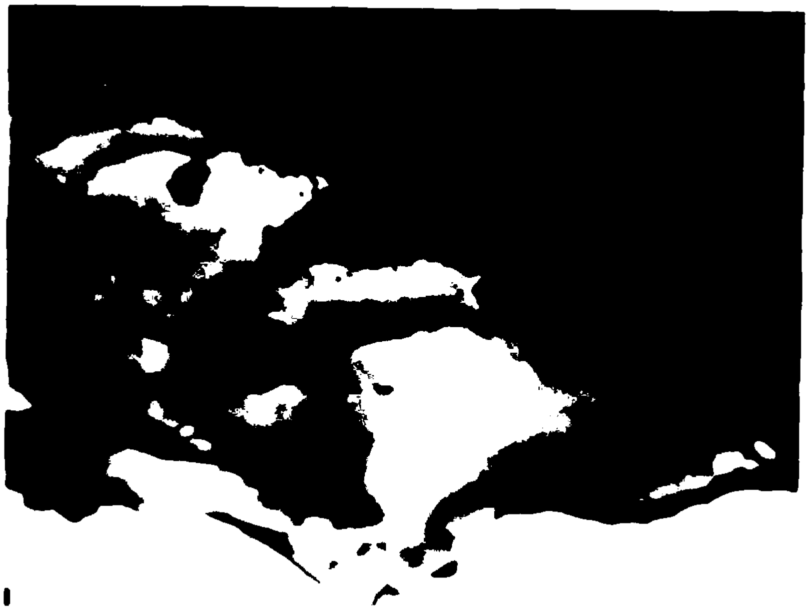

Figure 5 - Dark field TEM picture showing the presence of amorphous spheres.

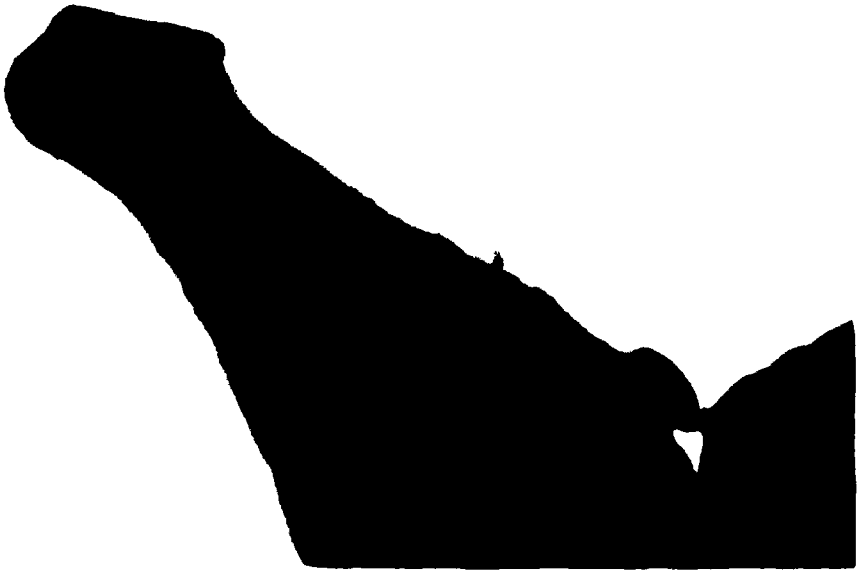

Figure 6 - Secondary phase separation observed in TEM.

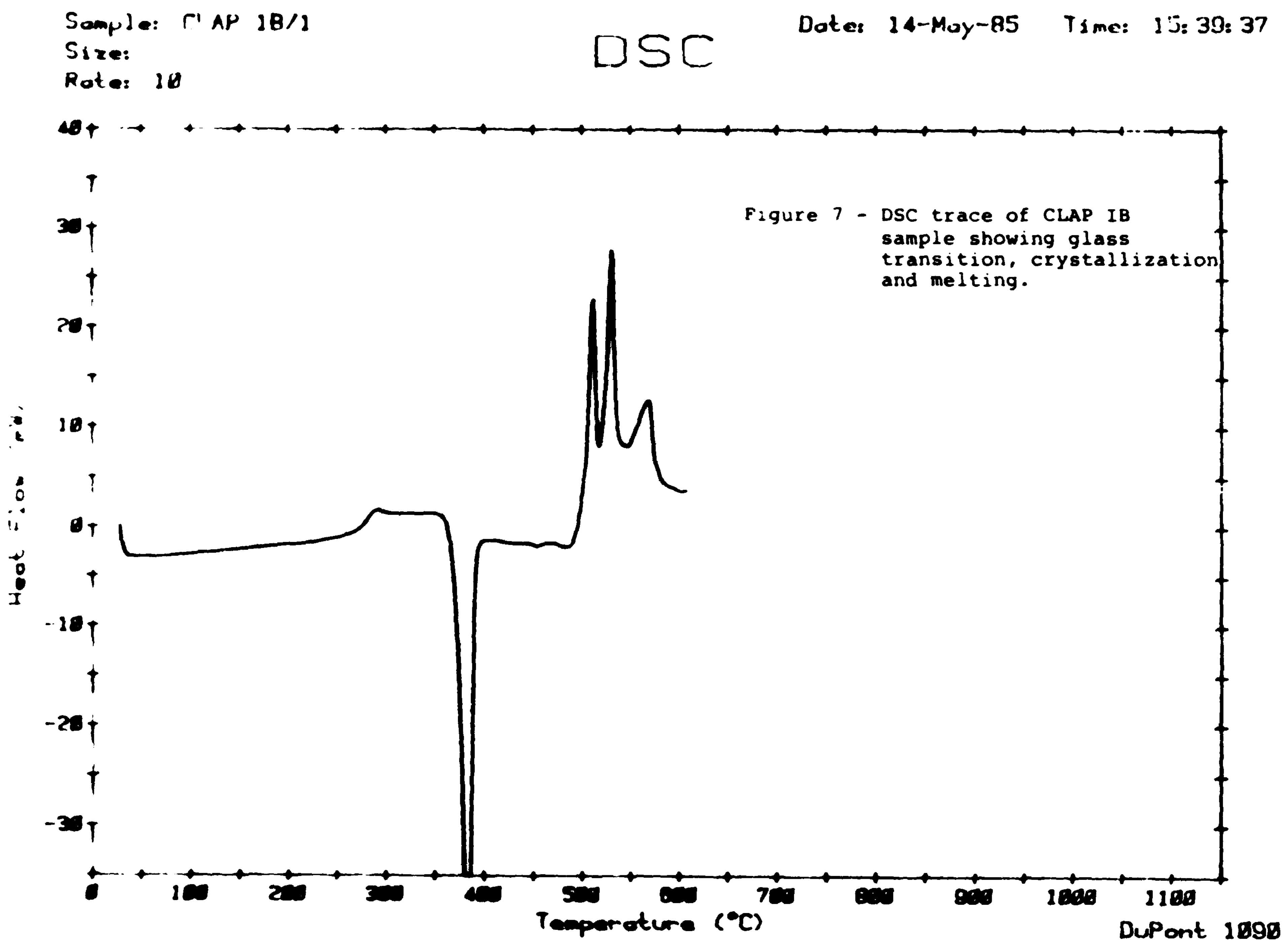

Figure 7 - DSC trace of CLAP IB sample showing glass transition, crystallization and melting.

Appendix

Extended abstract for submission to: 3rd International Symposium on Halide Glasses, Rennes, France, June 23-28, 1985.

IMMISCIBILITY AND CRYSTALLIZATION IN HEAVY METAL FLUORIDE GLASSES†

by

Osama H. El-Bayoumi,* Catherine J. Simmons,** Michael J. Suscavage,*
Edward M. Clausen, Jr.** and Joseph H. Simmons**

Heavy metal fluoride glasses are of considerable interest for use in optical communications because of their potential for low Rayleigh scattering at infrared wavelengths. However, this potentially high transparency can be substantially reduced by light scattering due to intrinsic microstructure in the glass. Crystallization and liquid-liquid immiscibility in HMF glasses are two sources of strong light-scattering which can be either wavelength dependent or independent, according to microstructure size and composition.

To date, only crystallization processes have received attention in HMF [illegible] et al. reported the possible observation of two amorphous [illegible] glass, using transmission electron [illegible] glass samples.[1] However, this structure [illegible]

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where both phases remain amorphous. The major problems arising in TEM studies of the phase-separation of glasses using replication techniques are the easy development of artifacts and the inability to test for crystallinity.

Studies of immiscibility transitions are very difficult in fluoride glasses for a number of reasons. First, crystallization rates are very fast and can rapidly overwhelm a liquid-liquid phase separation. Second, the presence of heavy metals in the glass composition combines with the low melting temperature of these glasses to cause melting of thin sections under observation in the electron microscope, making transmission electron microscopy [illegible].

In this paper, which is an expansion of work recently reported by [illegible], we present the first conclusive [illegible] of [illegible] liquid-liquid immiscibility in the system [illegible]. [illegible] derived from the combination of transmission electron [illegible] with [illegible] electron microscopy and x-ray [illegible] analysis, where [illegible] phases showing [illegible] diffraction are found [illegible].

[illegible]

Transmission electron microscopy revealed a wide range of microstructure sizes ranging down to 1500Å. Darkfield TEM studies of the droplet phase showed it to be amorphous. Under the electron beam, however, crystals appeared to form at the droplet sites and were then observed to melt and to form a homogenous glass. SEM studies showed that the observed crystals grow in the matrix phase at the droplet interface and grow to encapsulate it, while the droplet phase remains amorphous.

The phase equilibrium of this system, and the effect of the subliquidus immiscibility transition on crystallization kinetics are discussed.

References

1. [illegible] Osawa, T. Shibata, K. Nakamura and M. Kimura, "Light Scattering in [illegible] Fluoride Glasses." First International Symposium on Halide and Other Non-Oxide Glasses, Cambridge, UK, March [illegible], 19[illegible].

2. M. [illegible], O. H. El-Bayoumi, [illegible] and J. A. Harrington, "Observation of Phase Separation in Heavy Metal Fluoride Glass," Amer. Ceram. [illegible] 64 [illegible], [illegible] (19[illegible]).

3. M. [illegible] and O. H. El-Bayoumi, "Liquid-Liquid Phase Separation in Heavy Metal Fluoride Glass," to be published in Comm. Amer. Ceram. Soc.

4. [illegible], [illegible].

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